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RR-491 PCT/US

COVER GASES

Nigel Jeffrie RICKETTS
Malcolm Timothy FROST
Simon CASHION
Craig John KORN
Phillip Wilmott BAKER

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(71) Applicant (*for all designated States except US*): CAST CENTRE PTY LTD [AU/AU]; Cooper Road, St Lucia, QLD 4067 (AU).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): RICKETTS, Nigel, Jeffrie [AU/AU]; 7 Burke Place, Forest Lake, QLD 4078 (AU). FROST, Malcolm, Timothy [AU/AU]; 104 Creekside Street, Kenmore Hills, Queensland 4069 (AU). CASHION, Simon, Paul [AU/AU]; 41 Baty Street, St Lucia, QLD 4067 (AU). KORN, Craig, John [AU/AU]; 10 Aquamarine Street, Springfield, QLD 4300 (AU). BAKER, Phillip, Wilmott [AU/AU]; 23 Carrington Road, Indooroopilly, QLD 4068 (AU).

(74) Agent: GRIFFITH HACK; GPO Box 3125, Brisbane, Queensland 4001 (AU).

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(57) Abstract

A cover gas composition for protecting molten magnesium/magnesium alloy includes a fluorine containing inhibiting agent and a carrier gas. Each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for carbon di xide at a time horizon of 100 years) of less than 5000.

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COVER GASES

FIELD OF THE INVENTION

The present invention relates to compositions useful as cover gases for protecting molten magnesium/magnesium alloys. The present invention also relates to a method for protecting molten magnesium/magnesium alloys and to a method for extinguishing magnesium/magnesium alloy fires.

BACKGROUND ART

Magnesium is a highly reactive and thermodynamically unstable element. Molten magnesium is readily and violently oxidised in ambient air, burning with a flame temperature of approximately 2820°C. Three approaches have been used to inhibit the severe oxidation process. Salt cover fluxes may be sprinkled over the molten metal; oxygen may be excluded from contacting the molten metal by blanketing the molten metal with an inert gas such as helium, nitrogen or argon; or a protective cover gas composition may be used to blanket the molten metal. Protective cover gas compositions typically comprise air and/or carbon dioxide and a small amount of an inhibiting agent which reacts/interacts with the molten metal to form a film/layer on the molten metal surface which protects it from oxidation. To this day, the mechanism by which inhibiting agents protect molten reactive metals is not well understood.

US patent no. 1,972,317 relates to methods for inhibiting the oxidation of readily oxidisable metals, including magnesium and its alloys. The patent notes that at the time of its filing in 1932, numerous solutions had been proposed to the oxidation problem including displacing the atmosphere in contact with the metal with a gas such as nitrogen, carbon dioxide or sulphur dioxide. US 1,972,317 teaches inhibition of oxidation by maintaining in the atmosphere in contact with molten metal an inhibiting gas containing fluorine, either in elemental or combined form. Reference is made to many fluorine containing compounds with

the solids ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate or the gases evolved therefrom upon heating being said to be preferred. Notwithstanding the issue of US 1,972,317 in 1934, it was not until about the mid-1970's that a fluorine containing compound found commercial acceptance as an inhibiting agent in a cover gas.

Prior to about the mid-1970's, sulphur dioxide (SO_2) was widely used as an inhibiting agent in a magnesium cover gas composition but was replaced by sulphurhexafluoride (SF_6) which has become the industry standard. Typically, SF_6 based cover gas compositions contain 0.2-1% by volume SF_6 and a carrier gas such as air, carbon dioxide, argon or nitrogen. SF_6 has the advantages that it is a colourless, odourless, non-toxic gas which can be used for protecting molten magnesium/magnesium alloy and in the production of bright and shiny ingots with relatively low dross formation. However, SF_6 suffers from several disadvantages. Its sulphur based decomposition products at high temperature are very toxic. It is expensive, has limited sources of supply, and is one of the worst known greenhouse gases having a Global Warming Potential (GWP) at a time horizon of 100 years of 23,900 relative to 1 for carbon dioxide.

It is also noted that once magnesium has ignited, the resulting fire cannot be extinguished even with high concentrations of SF_6. SO_2 is even worse in this respect as it can accelerate a magnesium fire. The only known cover gas for extinguishing a magnesium fire is boron trifluoride (BF_3) which is very expensive and very toxic.

Alternative cover gas compositions are desirable.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a cover gas composition for protecting molten magnesium/magnesium alloy, the composition including a fluorine containing inhibiting agent and a carrier gas, wherein each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for

carbon dioxide at a time horizon of 100 years) of less than 5000.

Preferably, the inhibiting agent has minimal ozone depletion potential, more preferably the inhibiting agent has no ozone depletion potential.

Preferably, the inhibiting agent is non-toxic. In this regard, compounds having a Threshold Limit Value - Time Weighted Average (TLV-TWA) (the time weighted average concentration for a normal 8 hour workday and a 40 hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect) as issued by the American Conference of Governmental Industrial Hygienists of less than 100ppm are considered to be toxic. By way of example, BF_3, silicon tetrafluoride (SiF_4), nitrogen trifluoride (NF_3) and sulfuryl fluoride (SO_2F_2) disclosed in US 1972317 are toxic.

The composition may include a mixture of inhibiting agents (each having a GWP less than 5000) and preferably comprises a minor amount of inhibiting agent and a major amount of a carrier gas. Preferably, the composition consists of less than 1% by volume inhibiting agent and the balance carrier gas. More preferably, the composition contains less than 0.5% by volume (most preferably less than 0.1% by volume) inhibiting agent.

Preferably, each component of the composition has a GWP of less than 3000, more preferably, less than 1500.

Suitable carrier gases include air, carbon dioxide, argon, nitrogen and mixtures thereof.

The inhibiting agent may be selected from the group consisting of hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) and mixtures thereof. Preferably, the inhibiting agent has a boiling point of less than 100°C, more preferably less than 80°C. Where the inhibiting agent is gaseous at ambient temperature, it may be diffused in the carrier gas at the desired concentration. Where the inhibiting agent is liquid at ambient temperature, it may be entrained in the carrier gas to a desired concentration by

passing a flow of carrier gas over the inhibiting agent. Suitable hydrofluorocarbons and hydrofluoroethers are listed in Table 1 below which includes their boiling points (BP) and their GWP's (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) which have been sourced from IPCC 1996.

TABLE 1

Chemical Name	Industry Name	Formula	GWP	BP
difluoromethane	HFC-32	CH_2F_2	580	-52°C
pentafluoroethane	HFC-125	C_2HF_5	3,200	-49°C
1,1,1,2-tetrafluoroethane	HFC-134a, R134a	$C_2H_2F_4$	1,300	-26°C
difluoroethane	HFC-152a, R152a	$C_2H_4F_2$	140	-27°C
heptafluoropropane	HFC-227ea	C_3HF_7	2,900	-17°C
methoxy-nonafluorobutane	HFE-7100	$C_4F_9OCH_3$	480	61°C
ethoxy- nonafluorobutane	HFE-7200	$C_4F_9OC_2H_5$	90	78°C
dihydrodecafluoropentane	HFC-43-10-mee	$C_5H_2F_{10}$	1,300	54°C

A preferred cover gas composition consists of 1,1,1,2-tetrafluoroethane and dry air. Experimental work has demonstrated that such a cover gas composition provides protection at least the equal of SF_6 based compositions and can be utilised at lower concentrations of inhibiting agent. SF_6 has a GWP in excess of 18 times that of 1,1,1,2-tetrafluoroethane and is presently more than 2½ times the cost of 1,1,1,2-tetrafluoroethane.

In a second aspect, the present invention provides a method of protecting molten magnesium/magnesium alloy, the method including blanketing the molten magnesium/magnesium alloy with a cover gas composition according to the first aspect of the present invention.

The method according to the second aspect of the present invention is applicable to protecting molten magnesium/magnesium alloy in a foundry vessel such as a furnace and during casting.

In a third aspect, the present invention provides use of an inhibiting agent as defined with respect to the first aspect of the present invention for preventing or minimising oxidation of molten magnesium/magnesium alloy. By way of example, an inhibiting agent of the present invention may be used to prevent or minimise oxidation of molten magnesium/magnesium alloy during sand casting. Where the inhibiting agent is gaseous at ambient temperature, the sand mould may be purged with inhibiting agent prior to pouring of the molten metal. Where the inhibiting agent is liquid at ambient temperature, the sand mould may be sprayed with inhibiting agent from a squeeze bottle or the like prior to pouring of the molten metal. Other suitable methods of using inhibiting agents of the present invention to prevent or minimise oxidation of molten magnesium/magnesium alloy will be readily apparent to those of skill in the art of foundry practice.

In a fourth aspect, the present invention provides a method of extinguishing a magnesium/magnesium alloy fire, the method including exposing the fire to an atmosphere of

an inhibiting agent as defined with respect to the first aspect of the present invention. The fire may be so exposed by, for example, subjecting it to a flow of the inhibiting agent or immersing it in a reservoir containing the inhibiting agent.

EXAMPLES

The ensuing non-comparative Examples are illustrative of preferred embodiments of the present invention and are not to be construed as limiting the scope of the present invention in any way.

Example 1

A crucible furnace containing 100 grams of molten pure magnesium at 680°C was blanketed with a gaseous composition consisting of 0.02% by volume 1,1,1,2-tetrafluoroethane and the balance dry air. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

Comparative Example 1

Comparative Example 1 was identical to Example 1 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF_6. Good molten magnesium protection was not observed, and the magnesium sample burned rapidly. Adequate protection of the molten magnesium sample was only achieved when the gaseous composition consisted of 0.05% by volume SF_6 and the balance dry air. At this concentration of SF_6 deliberate rupturing of the surface film resulted in localised burning of the molten magnesium sample.

Example 1 and Comparative Example 1 demonstrate that the inventive cover gas composition provides good protection of molten magnesium at a lower concentration than an SF_6 based composition.

Example 2

A series of single ingots of both pure magnesium and magnesium-aluminium alloy AZ91 were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with a cover gas composition, and the molten metal was allowed to solidify. In the case of AZ91 alloy the cover gas composition consisted of 0.04% by volume 1,1,1,2-tetrafluoroethane and the balance dry air. The cover gas composition for the pure magnesium casting consisted of 0.1% by volume 1,1,1,2-tetrafluoroethane and the balance dry air.

Single ingots of both pure magnesium and AZ91 alloy were produced free of burning, with bright shiny surface finishes, with very low levels of dross, and with no reaction with boron nitride mould coatings.

Comparative Example 2

Comparative Example 2 was identical to Example 2 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF_6 which was used at the same concentrations, ie. 0.04% by volume in dry air for AZ91 alloy and 0.1% by volume in dry air for pure magnesium.

The ingots produced in Example 2 had lower levels of dross and had a more attractive surface finish than those produced in Comparative Example 2.

Example 3

A small flow of 1,1,1,2-tetrafluoroethane was continuously metered into a container that is used to collect molten magnesium dross. During transport of the dross from the furnace to the container, the dross contacted the air and ignited. Upon placing the dross into the container, the burning quickly stopped.

Comparative Example 3

Comparative Example 3 was identical to Example 3 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF_6. In this case, the dross continued to burn after being placed into the container.

Example 3 and Comparative Example 3 demonstrate that an inhibiting agent of the present invention is able to suppress the burning of magnesium metal/dross. This enables minimisation of magnesium fume in a working environment and prevention of oxidation of the magnesium metal content in the dross. This would enable dross processing operations to recover valuable magnesium metal content.

Example 4

Ingots of pure magnesium were cast in 8kg ingot moulds on an industrial-sized ingot casting machine having a controllable atmosphere chamber. The casting machine was operated at a casting rate of 3 tonnes of cast metal per hour with 330 litres per minute dry air and 3.3 litres per minute 1,1,1,2-tetrafluoroethane introduced into the chamber. Ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

Comparative Example 4

Comparative Example 4 was identical to Example 4 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF_6 which was used at the same flow rate and at the same concentration in dry air. Ingots produced in Comparative Example 4 exhibited similar properties to those produced in Example 4.

Example 4 and Comparative Example 4 demonstrate that the inventive gas can successfully replace SF_6 for industrial scale continuous production of magnesium ingot.

Example 5

A series of single ingots of pure magnesium were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with cover gas composition, and the molten metal was allowed to solidify. The cover gas composition was produced by passing 0.5 litres per minute of dry air over 50ml of the HFE liquid methoxy-nonafluorobutane. The resulting gas phase mixture flowed to the single ingot casting apparatus. Single ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

Example 6

A series of single ingots of pure magnesium were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with a cover gas composition, and the molten metal was allowed to solidify. The cover gas composition was produced by passing 0.5 litres per minute of dry air over 50ml of the HFC liquid dihydrodecafluoropentane. The resulting gas phase mixture flowed to the single ingot casting apparatus. Single ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

Example 7

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.6 litres per minute of dry air over 50ml of the HFE liquid methoxy-nonafluorobutane. The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed.

with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

Example 8

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.9 litres per minute of dry air over 50ml of the HFE liquid ethoxy-nonafluorobutane. The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

Example 9

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.9 litres per minute of dry air over 50ml of the HFC liquid dihydrodecafluoropentane. The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

Example 10

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a gaseous composition consisting of 0.4% by volume difluoroethane and the balance dry air. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

Comparative Example 10

Comparative Example 10 was identical to Example 10 with the exception that difluoroethane was replaced by SF_6 which was used at the same concentration. Good molten magnesium protection was observed.

Example 10 and Comparative Example 10 demonstrate that an inhibiting agent of the present invention provides equivalent protection of molten magnesium metal compared to SF_6.

Example 11

Magnesium squeeze-castings were produced by hand-pouring molten magnesium into the shot sleeve of a vertical injection squeeze casting machine. Prior to pouring the molten magnesium into the shot sleeve, a small volume of pure 1,1,1,2-tetrafluoroethane was introduced into the shot sleeve. This protected the molten magnesium in the shot sleeve and prevented the molten magnesium from burning during the filling of the mould.

Example 12

Various magnesium components were produced using the investment casting technique. Prior to filling the investment casting shell with molten magnesium, the shell was purged with pure 1,1,1,2-tetrafluoroethane. This prevented the magnesium from burning while solidifying inside the shell. Upon cooling, the shell mould was removed. The magnesium casting exhibited a good surface finish.

Example 13

Various magnesium components were produced using the sand casting technique. Prior to filling the sand mould with molten magnesium, the sand mould was purged with pure

1,1,1,2-tetrafluoroethane. This prevented the magnesium from burning while solidifying inside the sand mould. Upon cooling, the sand mould was removed. The magnesium casting exhibited a good surface finish.

Example 14

A melt furnace having a diameter of 1.6 metres and containing 4 tonnes of molten pure magnesium was blanketed with 60 litres per minute dry air and 0.6 litres per minute 1,1,1,2-tetrafluoroethane. Good molten magnesium protection was observed, with the formation of a thin protective surface film.

Comparative Example 14

Comparative Example 14 was identical to Example 14 with the exception that 1,1,1,2-tetrafluorethane was replaced by SF_6 at differing flow rates. The flow rate of dry air was maintained at 60 litres per minute. Good molten magnesium protection was only achieved at an SF_6 flow rate of 2 litres per minute.

Example 14 and Comparative Example 14 demonstrate that the inventive cover gas composition provides good industrial scale protection of molten magnesium at a lower concentration than an SF_6 based composition.

CLAIMS

1. A cover gas composition for protecting molten magnesium/magnesium alloy, the composition including a fluorine containing inhibiting agent and a carrier gas, wherein each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) of less than 5000.

2. A composition as claimed in claim 1 wherein the inhibiting agent has no ozone depletion potential.

3. A composition as claimed in claim 1 or claim 2 wherein the carrier gas is selected from the group consisting of air, carbon dioxide, argon, nitrogen and mixtures thereof.

4. A composition as claimed in any one of the preceding claims wherein each component of the composition has a GWP of less than 3000.

5. A composition as claimed in any one of the preceding claims wherein the inhibiting agent is selected from the group consisting of hydrofluorocarbons, hydrofluoroethers and mixtures thereof.

6. A composition as claimed in any one of the preceding claims wherein the inhibiting agent has a boiling point of less than 100°C.

7. A composition as claimed in any one of the preceding claims wherein the inhibiting agent is selected from the group consisting of difluoromethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane, difluoroethane, heptafluoropropane, methoxy-nonafluorobutane, ethoxy-nonafluorobutane,

dihydrodecafluoropentane and mixtures thereof.

8. A composition as claimed in any one of the preceding claims wherein each component of the composition has a GWP of less than 1500.

9. A composition as claimed in any one of the preceding claims wherein the inhibiting agent is 1,1,1,2-tetrafluoroethane and the carrier gas is dry air.

10. A composition as claimed in any one of the preceding claims containing less than 1% by volume inhibiting agent.

11. A composition as claimed in claim 10 containing less than 0.5% by volume inhibiting agent.

12. A composition as claimed in claim 11 containing less than 0.1% by volume inhibiting agent.

13. A cover gas composition substantially as herein described in any non-comparative Example.

14. A method of protecting molten magnesium/magnesium alloy, the method including blanketing the magnesium/magnesium alloy with a cover gas composition as claimed in any one of the preceding claims.

15. Use of an inhibiting agent as defined in any one of claims 1-12 for preventing or minimising oxidation of molten magnesium/magnesium alloy.

16. A method of extinguishing a magnesium/magnesium alloy fire, the method including exposing the fire to an atmosphere of an inhibiting agent as defined in any one of claims 1-12.

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To:

GRIFFITH HACK
GPO Box 3125
BRISBANE QLD 400.

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

	Date of mailing *(day/month/year)* 16 JUN 2000
Applicant's or agent's file reference FP12616	**FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/AU00/00393	International filing date 28 April 2000
Applicant CAST CENTRE PTY LTD et al	

1. [X] The applicant is hereby notified that the international search report has been established and is transmitted herewith

Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

[ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

[ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau.

If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later)

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	B. PREMARATNE

(See notes on accompanying sheet)

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

(i) the claim is unchanged;
(ii) the claim is cancelled;
(iii) the claim is new;
(iv) the claim replaces one or more claims as filed;
(v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."

2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."

3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."

4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under Article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequences if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments and any accompanying statement, under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the time of filing the amendments (and any statement) with the International Bureau, also file with the International Preliminary Examining Authority a copy of such amendments (and of any statement) and, where required, a translation of such amendments for the procedure before that Authority (see Rules 55.3(a) and 62.2, first sentence). For further information, see the Notes to the demand form (PCT/IPEA/401).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see the *PCT Applicants Guide*, Volume II.

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under Article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule" and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasised that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, eg. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Preliminary Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When? Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How? Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00393

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: B22D 21/04, 21/02; A62D1/02; C22B 26/22, 4/02; C22C 1/02, 23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: B22D 21/04, 21/02; A62D1/02; C22B 26/22, 4/02; C22C 1/02, 23/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI - Key words: fluoro:

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96/22129 A (Minnesota Mining and Manufacturing Company) 25 July 1996 (see page 7, line 21 to last line; page 12, lines 21 to 23; page 14 lines 2 to 7)	1-8,10-12
X	US 5115868 A (Dougherty, Jr. et al.) 26 May 1992 (see col 2, line 65 to col 3, line 33; col 4, lines 31 to 38;Example 1, Example 5)	1-13
X	WO 91/02564 A (Great Lakes Chemical Corporation) 7 March 1991 (see page 4, lines 1 to 20; page 7, lines19 to 25)	1-8, 10-12
A	US 5855647 A (Li et al.) 5 January 1999 (see the entire document)	1-16

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 June 2000	16 JUN 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer B. PREMARATNE

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00393

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4214899 A (Radzilowski) 29 July 1980 (see the entire document)	1-16
A	Derwent Abstract Accession No. 96-319293/32, class M25, JP, A, 08143985 (Tokai Rika Denki KK) 4 June 1996 (see the whole abstract)	1-16

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00393

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	9622129	CA	2210994	CN	1176606	EP	804264
		US	5718293	US	5919393		
US	5115868	AU	66199/90	BR	9007709	CA	2067385
		CN	1051126	EP	494987	EP	592019
		GR	90100731	US	5040609	ZA	9007929
		WO	9104766				
WO	9102564	AU	61719/90	BR	9006888	CA	2023333
		EP	439579	IL	95365	NO	911579
		ZA	9006427	US	5124053	AU	66152/90
		CA	2027273	CS	9004908	EP	447538
		WO	9105585	CN	1051513	AU	73400/91
		CA	2036563	CN	1054544	US	5113947
		WO	9112853	ZA	9101290	ZA	9007937
US	4214899	AU	55171/80	BR	8000791	CA	1162746
		DK	310/80	EP	16671	ES	488307
		ES	8102199	ES	494995	ES	494996
		ES	8105038	ES	8105039	FI	800682
		JP	55125214	NO	800150	YU	634/80
		ZA	8000277				
US	5855647	CA	2237748				

END OF ANNEX

PATENT COOPERATION TREA

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference FP12616	FOR FURTHER ACTION	See Notification of Transmittal f International Preliminary Examination Report (Form PCT/IPEA/416).
International Application No. PCT/AU00/00393	International Filing Date *(day/month/year)* 28 April 2000	Priority Date *(day/month/year)* 28 April 1999
International Patent Classification (IPC) or national classification and IPC Int. Cl. [7] B22D 21/04, 21/02; A62D 1/02; C22B 26/22, 4/02, C22C 1/02, 23/00		
Applicant CAST CENTRE PTY LTD et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheet(s).

3. This report contains indications relating to the following items:

I	☒	Basis of the report
II	☐	Priority
III	☐	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	☐	Lack of unity of invention
V	☒	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	☐	Certain documents cited
VII	☐	Certain defects in the international application
VIII	☐	Certain observations on the international application

Date f submission of the demand 19 October 2000	Date of completion of the report 5 September 2001
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer B. PREMARATNE

INTERNATIONAL PRELI[illegible]ARY EXAMINATION REPORT

[illegible]ternational application No.
PCT/AU00/00393

I. Basis of the rep rt

1. With regard to the elements of the international application:*

[X] the interna[illegible]al application as originally filed.

[ ] the description, pages , as originally filed,
pages , filed with the demand,
pages , received on with the letter of

[ ] the claims, pages , as originally filed,
pages , as amended (together with any statement) under Article 19,
pages , filed with the demand,
pages , received on with the letter of

[ ] the drawings, pages , as originally filed,
pages , filed with the demand,
pages , received on with the letter of

[ ] the sequence listing part of the description:
pages , as originally filed
pages , filed with the demand
pages , received on with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language which is:

[ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

[ ] the language of publication of the international application (under Rule 48.3(b)).

[ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, was on the basis of the sequence listing:

[ ] contained in the international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readable form.

[ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. [ ] The amendments have resulted in the cancellation of:

[ ] the description, pages

[ ] the claims, Nos.

[ ] the drawings, sheets/fig.

5. [ ] This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/AU00/00393

V. **Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims 14 - 16	YES
	Claims 1 - 13	NO
Inventive step (IS)	Claims 14 - 16	YES
	Claims 1 - 13	NO
Industrial applicability (IA)	Claims 1 - 16	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)

NOVELTY : Claims 1 - 13

D1= WO 9622129

D2= US 5115868

D3= WO 9102564

The invention disclosed in claims 1-13 is not novel in the light of the documents D1-D3.

The above documents disclose fire extinguishing compositions comprising hydrofluorocarbons and hydrofluoroethers having no ozone depletion potential and having a global warming potential of less than 5000.The disclosed compounds have boiling points less than 100°C and are used mixed with an inert carrier gas. These compositions are considered to be suitable for protection of molten magnesium/magnesium alloys.

INVENTIVE STEP

Claims 1-13: as above